



## DECLARATION

I, Junko Nakamura, of SHIGA INTERNATIONAL PATENT OFFICE, 3-1, Yaesu 2-chome, Chuo-ku, Tokyo, Japan, understand both English and Japanese, am the translator of the English document attached, and do hereby declare and state that the attached English document contains an accurate translation of the official certified copy of Japanese Patent Application No. 11-341444 and that all statements made herein are true to the best of my knowledge.

Declared in Tokyo, Japan

This 24th day of November, 2004

Junko Nakamura

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PATENT OFFICE  
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this office.

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Application Number: Patent Application No. 11-341444  
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Mitsubishi Gas Chemical Co., Inc.

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[Title of the Invention] METHOD FOR STOPPING METHANOL  
REFORMING APPARATUS

[Number of Claims] 3

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[Item]	Specification	1
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[Item]	Drawing	1
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[Item]	Abstract	1
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[Document type] Specification

[Title of the Invention] METHOD OF STOPPING METHANOL REFORMING  
APPARATUS

[Claims]

[Claim 1] A method of stopping a methanol reforming apparatus that generates a hydrogen-rich gas by reacting a mixed gas of water, methanol and air on a catalyst, which comprises:

stopping the introduction of air to thereby lower the catalyst temperature through a steam reforming reaction, stopping the introduction of water and methanol while the catalyst is still hotter than 100°C, and adjusting the methanol concentration to 18% by mole or lower.

[Claim 2] A method of stopping a methanol reforming apparatus according to claim 1, wherein air is introduced again after bringing the methanol concentration to 18% by mole or lower, then remaining water and methanol are evaporated and removed by means of the oxidization heat of the catalyst.

[Claim 3] A method of stopping a methanol reforming apparatus according to claim 2, wherein air at a temperature of 100°C or lower is introduced after removing water and methanol by evaporation, and then the catalyst is cooled down and the gas is purged.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to method of stopping a methanol reforming apparatus that generates a hydrogen enriched gas from water and methanol.

[0002]



[Prior Art]

Fuel cells have been developed as a means for driving low-pollution vehicles and for supplying electric power to vehicles.

Hydrogen in the form of a compressed hydrogen gas or liquid hydrogen is convenient as the energy source for the fuel cell, but there are problems regarding to safety and the ease of handling. Thus there is a demand for a hydrogen supply apparatus having higher safety.

Recently, technologies for preparing hydrogen enriched gas by reforming alcohol or hydrocarbons using a catalyst have been intensively studied and developed, and various catalysts and reaction apparatuses have been invented.

[0003]

[Problem to be Solved by the Invention]

However, when methanol, which has a low flash point and a low ignition point, is reformed by a methanol reforming apparatus, particularly when employing the autothermal reaction process, wherein a partial oxidization reaction and steam reforming reaction are carried out at the same time, methanol vapor and air coexist on a catalyst that has a high temperature, the mixing ratio of water, methanol and air must not be within a range in which the reaction proceeds at an excessively high rate (hereinafter this range is referred to as "high-rate reaction region"), and the amounts of these materials to be introduced must be strictly controlled.

[0004]

On the other hand, stopping the operation of the methanol reforming apparatus, the supplies of water, methanol and air are stopped and the catalyst layer is cooled. However, if an excessive amount of air is supplied during the autothermal reaction

process, a partial oxidization reaction proceeds, thus giving rise to the possibility of an uncontrolled thermal runaway of the catalyst layer. Therefore, when stopping the methanol reforming apparatus, it is also important to strictly control the mixing ratio of water, methanol and air so as to avoid the high-rate reaction region.

[0005]

Also, if water and methanol used as the fuel remain in the apparatus when restarting a methanol reforming apparatus that has been stopped, the remaining fuel will deviate the mixing ratio of water, methanol and air when starting the operation, thus giving rise to the possibility of thermal runaway of the catalyst.

Therefore, the operation of stopping the methanol reforming apparatus must be carried out while paying attention to the mixing ratio of water, methanol and air, and the fuel must not be allowed to remain in the apparatus. Thus, the stopping operation takes a long time and requires a complicated control procedure.

[0006]

The present invention has been made in consideration of the problems described above, and an object thereof is to quickly cool down the catalyst layer while preventing thermal runaway from occurring and removing the remaining fuel when stopping the operation of the methanol reforming apparatus.

[0007]

[Means for Solving the Problem]

With the present invention, in order to achieve the objects described above, first the introduction of air is stopped while the introduction of water and methanol to the catalyst layer (reforming catalyst 41 in FIG. 1) is continued, to thereby lower the catalyst layer temperature by making use of the endothermic effect of the methanol steam

reforming reaction.

The introduction of air may be stopped either quickly by means of a shut-off valve or gradually by means of a control valve or the like.

[0008]

When the catalyst layer has been cooled down to a predetermined temperature, the introduction of water and methanol is stopped.

Provided that the operation described above is carried out while the catalyst layer temperature is 100°C or higher, the methanol steam reforming reaction can be effectively continued by using the residual heat of the catalyst layer.

Consequently, the cooling of the catalyst layer is accelerated and the methanol concentration in the mixed gas can be lowered quickly to 18% by mole or less, which is outside of the high-rate reaction region.

[0009]

The present inventors found, from the three-component mixture phase diagram of water, methanol and air shown in FIG. 2, that the reaction does not proceed at a high rate when the methanol concentration in the mixed gas is 18% by mole or less. In this drawing, the hatched portion shows the high-rate reaction region.

Therefore, the water and methanol that remain in the apparatus (hereinafter sometimes referred to as “residual fuel”) can be evaporated and removed by reintroducing air into the catalyst layer to oxidize the catalyst and utilizing the oxidization heat generated thereby, after the methanol concentration in the mixed gas has decreased to 18% by mole or less.

[0010]

Once the residual fuel has been removed by the operation described above, the

catalyst temperature can be lowered quickly without causing dew condensation even when cool air at a temperature lower than 100°C is introduced into the catalyst.

Also because the residual fuel gas, too, is purged from the apparatus by the cool air, the possibility of the amount of the mixture of water, methanol and air introduced deviating from the set value when restarting the operation can be effectively avoided.

[0011]

Preferred embodiments of the present invention will now be described below with reference to the accompanying drawings.

FIG. 1 shows a system for supplying fuel to a fuel cell in an electric vehicle, where the reference numeral 10 denotes a fuel cell.

The fuel cell 10 generates electricity by using hydrogen and oxygen that is taken from air as the fuel.

A hydrogen supply system and an air supply system for the fuel cell 10 will be described below.

[0012]

[Hydrogen supply system]

The hydrogen supply system comprises a combustion device 21, an evaporator 22, a reformer (methanol reforming apparatus) 23, a CO eliminator 24, a starting heater 25, heat exchangers 26a, 26b, mixed water-methanol solution tanks 27a, 27b and a methanol tank 28 as major components.

[0013]

The combustion device 21 has an electric heater 31 serving as an ignition device, a combustion catalyst 32 that maintains the state of combustion and a temperature sensor 33 that monitors the temperature inside of the apparatus, wherein methanol supplied

from the methanol tank 28 is burned with the air supplied from the air supply system, thereby generating a combustion gas used to warm up the evaporator 22 which evaporates the mixed water-methanol solution that is supplied to the evaporator 22.

[0014]

Connected to the combustion device 21 is an off gas tube 34 provided for the purpose of reusing the off gas that includes hydrogen-rich gas, which is generated in the reformer 23 in the period from the startup to the normal operation, and unreacted hydrogen, which is discharged from the fuel cell 10 during stationary operation, as the fuel for combustion.

[0015]

In the evaporator 22, the mixed water-methanol solution that has been supplied from the mixed water-methanol solution tank 27a where the S/C ratio is controlled to 1.5 or from the mixed water-methanol solution tank 27b where the S/C ratio is controlled to 4.6 is sprayed from a nozzle and evaporated by the combustion gas supplied from the combustion device 21, thereby generating the mixed water-methanol gas.

The evaporator 22 is provided with a temperature sensor 36 for monitoring the temperature inside of the device.

[0016]

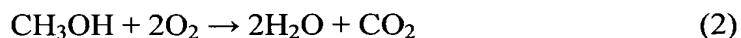
Installed in the reformer 23 is a reforming catalyst 41 comprising a honeycomb structure of which surface is coated with a catalyst such as Ni, Ru, Rh, Cu-Zn or the like, so that the mixed water-methanol gas supplied from the evaporator 22 is brought onto the reforming catalyst layer 41 to generate hydrogen-rich gas.

The reforming catalyst layer 41 has an O<sub>2</sub> sensor 42 installed at the inlet thereof, and a temperature sensor 43 and a methanol sensor not shown in the drawing installed

inside of the reforming catalyst layer 41.

[0017]

In the reformer 23, the autothermal reforming reaction takes place as follows.



The reaction scheme (1) represents the steam reforming reaction by methanol and water that produces the target product of hydrogen.

The reaction scheme (2) represents the reaction of partial oxidization of methanol that produces heat by oxidization reaction which provides for the heat needed in the endothermic reaction represented by reaction scheme (1).

[0018]

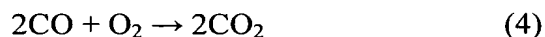
In the reformer 23, in addition to the reactions represented by the reaction schemes (1) and (2), a trace amount of carbon monoxide is generated in an inevitable reaction of methanol decomposition represented as follows.



The carbon monoxide deteriorates Pt catalyst provided in the fuel cell 10 and leads to lower efficiency of power generation and shortens the service life of the cell, and is therefore removed by the CO eliminator 24 installed in a latter stage.

[0019]

The CO eliminator 24 has a selective oxidization catalyst layer made by coating the surface of a honeycomb structure with a catalyst such as Pt or Ru. When hydrogen-rich gas generated by the reformer 23 is supplied, the carbon monoxide is removed from the hydrogen-rich gas in the following reaction of selective oxidization of CO.



[0020]

Installed between the reformer 23 and the CO eliminator 24 is the heat exchanger 26a provided for the purpose of cooling down the hydrogen-rich gas generated by the reformer 23 thereby protecting the selective oxidization catalyst in the CO eliminator 24 from thermal damage. Similarly installed between the CO eliminator 24 and the fuel cell 10 is the heat exchanger 26b provided for the purpose of cooling down the hydrogen-rich gas supplied from the CO eliminator 24 thereby protecting the Pt catalyst in the fuel cell 10 from thermal damage.

[0021]

Valves 51, ..., pumps 55, ... installed in the hydrogen supply system are controlled by an ECU (Electronic Control Unit) 45.

The ECU 45 sends command signals to the valves 51, ..., the pumps 55, ... in accordance to the output signals from the O<sub>2</sub> sensor 42 and the temperature sensor 43 and a stop command, thereby causing these devices to function.

[0022]

(Air supply system)

The air supply system comprises a PCU 61, a drive motor 62, a super charger 63, an inter cooler 64 and filters 65a, 65b as major components, and supplies air, that is introduced from the outside, to the fuel cell 10, the combustion device 21 and the starting heater 25.

Main function of the PCU 61 is to adjust the output of the drive motor 62, by regulating the electric power supplied from the fuel cell 10 and supplies the regulated power to the drive motor 62.

[0023]

The super charger 63 compresses the air taken from the outside through the filter 65a, via a resonator 66.

The inter cooler 64 is provided for cooling down the air that has been heated through compression by the super charger 63. The cooled air passes through the filter 65b, which is installed in the latter stage of the inter cooler 64, and is supplied to the fuel cell 10, the combustion device 21 and the starting heater 25.

[0024]

A method of stopping the reformer 23 according to the present embodiment will now be described below. Before the description, an example of steady operation (normal reforming operation) will be outlined.

During steady operation, the valve 50 is open so that air from the air supply system, namely the air that has been introduced through the resonator 66 and the filter 65a, cooled by the inter cooler 64 and has passed through the filter 65b, is supplied to the combustion device 21 and the evaporator 22, the reformer 23, ..., that are installed in the latter stage thereof.

[0025]

With the valve 51 being closed and the valve 52 open, the pump 56 supplies the mixed water-methanol solution with the S/C ratio controlled to 1.5 from the mixed water-methanol solution tank 27a to the evaporator 22, so that the mixed water-methanol solution is sprayed from the nozzle into the evaporator 22.

In the evaporator 22, the mixed water-methanol solution is evaporated by the combustion gas supplied from the combustion device 21, thereby generating the mixed water-methanol gas which is supplied to the reformer 23.

[0026]



In the reformer 23, the mixed water-methanol gas is passed through the reforming catalyst 41 to produce hydrogen-rich gas through the reactions of the reaction schemes (1) and (2).

The hydrogen-rich gas produced in the reformer 23 is cooled down from about 300°C to about 100°C while passing through the heat exchanger 26a, to be supplied to the CO eliminator 24.

In the CO eliminator 24, carbon monoxide is removed in the reaction of the reaction scheme (4) by passing the hydrogen-rich gas through the selective oxidization catalyst layer.

[0027]

The hydrogen-rich gas with CO removed therefrom is cooled down from about 180°C to about 80°C while passing through the heat exchanger 26b, and is then supplied to the fuel cell 10.

In the fuel cell 10, the hydrogen-rich gas supplied from the hydrogen supply system and air supplied from the air supply system are used to generate electricity.

While the fuel cell 10 discharges the off gas that includes unreacted hydrogen, the off gas is returned through an off gas tube to the combustion device 21 and is reused as the fuel of combustion.

[0028]

A method of stopping the reformer 23 in steady reforming operation will now be described below.

This reformer stopping method comprises a first step in which the introduction of air to the reformer 23 is stopped, a second step in which the introduction of mixed water-methanol gas to the reformer 23 is stopped, a third step in which air is introduced again,

and a fourth step in which air of a temperature of 100°C or lower is introduced.

[0029]

In the first step, the valve 50 that has been open during the steady operation is closed.

This shuts off the introduction of air from the air supply system to the hydrogen supply system, namely to the combustion device 21 and the evaporator 22, the reformer 23, ..., that are installed in the latter stage thereof.

At this time, since the ratio of air in the mixture decreases in comparison to water and methanol in the reformer 23, the endothermic reaction of the reaction scheme (1) proceeds while the exothermic reaction of the reaction scheme (2) is suppressed. As a result, the reforming catalyst layer 41 is effectively cooled.

[0030]

In the second step, the valve 52 that has been open during the steady operation is closed while the reforming catalyst layer 41 which is being cooled is still hotter than 100°C.

Temperature of the reforming catalyst layer 41 is constantly monitored by a temperature sensor 43 installed therein, and the ECU 45 controls the valve 52 to close according to the signal from the temperature sensor 43.

[0031]

This shuts off the supply of the mixed water-methanol solution from the mixed water-methanol solution tank 27a to the evaporator 22 and stops the introduction of the mixed water-methanol gas to the reformer 23.

Even after the introduction has been stopped, the steam reforming reaction is effectively continued by making use of the residual heat of the reforming catalyst layer

41, thereby accelerating the cooling of the reforming catalyst layer 41. At the same time, methanol concentration in the mixed gas quickly decreases to 18% by mole or lower, clear of the high-rate reaction region.

[0032]

Next in the third step, when methanol concentration has decreased to 18% by mole or lower, the valve 50 that was closed in the first step is opened.

The methanol concentration is monitored by the methanol sensor installed in the reforming catalyst layer 41, and the ECU 45 controls the valve 50 to open according to the signal from the methanol sensor.

[0033]

This causes air from the air supply system to be introduced again into the reforming catalyst 41, so that the catalyst is oxidized and refreshed.

Water and methanol that remain in the reformer 23, namely the residual fuel, are evaporated and removed by the oxidization heat generated when the catalyst is oxidized.

It is made possible to introduce the air again in the third step because the methanol concentration is 18% by mole or lower, clear of the high-rate reaction region.

[0034]

Last, in the fourth step, air that has been cooled down to 100°C or lower while passing through the inter cooler 64 in the air supply system is introduced into the reforming catalyst layer 41.

At this time, since the residual fuel has been effectively removed in the third step, the catalyst can be cooled down quickly by the cold air without causing dew condensation.

Moreover, since the residual fuel gas is purged at the same time, a trouble such as

alteration in the mixing ratio of water, methanol and air when restarting the operation can be effectively avoided.

[0035]

[Advantage Effects of the Invention]

The present invention has the following effects.

(a) The introduction of water and methanol is stopped while the catalyst layer temperature is 100°C or higher after the introduction of air has been stopped and the catalyst temperature has decreased due to the steam reforming reaction when stopping the operation of the methanol reforming apparatus. Thus the methanol steam reforming reaction can be effectively continued by using the residual heat of the catalyst layer.

Consequently, the cooling down of the catalyst layer is accelerated and the methanol concentration in mixed gas can be lowered quickly to 18% by mole or less, which is outside of the high-rate reaction region.

[0036]

(b) If air is reintroduced after lowering the methanol concentration to 18% by mole or less and water and methanol that remain in the apparatus are evaporated and removed by utilizing the oxidization heat generated as the catalyst is oxidized, the possibility of altering the mixing ratio of water, methanol and air during start-up can be effectively avoided.

[0037]

(c) If air at a temperature of 100°C or lower is introduced after removing water and methanol by evaporation, the catalyst temperature can be lowered quickly without causing dew condensation.

Also because the introduction of air purges the residual fuel from the apparatus,

the possibility of altering the mixing ratio can be effectively avoided.

[Brief Description of the Drawings]

[FIG. 1] FIG. 1 shows a system for supplying fuel to a fuel cell in an electric vehicle according to the embodiment of the present invention.

[FIG. 2] FIG. 2 is a three-component mixture phase diagram of water, methanol and air.

[Description of Reference Symbols]

23: reformer ( methanol reforming apparatus); 41: reforming catalyst

[Document Type] Abstract

[Abstract]

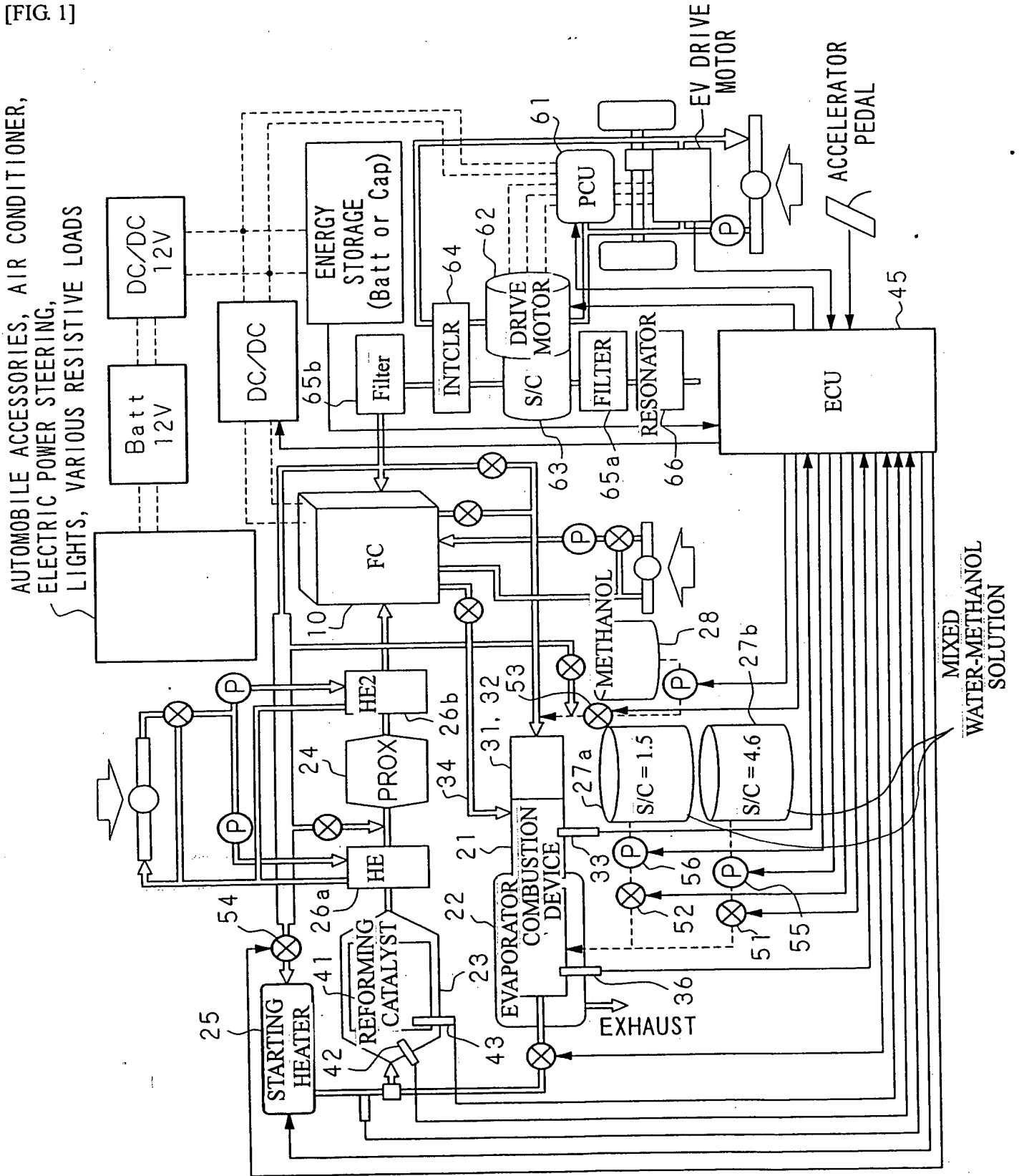
[Problem to be Solved by the Invention] To quickly cool down the catalyst layer while preventing thermal runaway from occurring and removing the remaining fuel when stopping the operation of the methanol reforming apparatus.

[Means for Solving the Problem] Operation of the methanol reforming apparatus (23) is stopped by first stopping the introduction of air, and a steam reforming reaction which is an endothermic reaction proceeds while suppressing a partial oxidization reaction which is an exothermic reaction. Next the introduction of water and methanol is stopped while the catalyst layer temperature is 100°C or higher. Next air is reintroduced after lowering the methanol concentration to 18% by mole or less. The water and methanol that remain in the apparatus (23) are evaporated and removed by utilizing the oxidization heat generated as the catalyst is oxidized by the reintroducing of the air. After removing water and methanol, air at a temperature of 100°C or lower is introduced so that the catalyst is cooled and the apparatus is purged.

[Selected Drawing] FIG. 1



[FIG. 1]





Docket Number J81062A1  
[Document Type] Drawing

Page (2)

[FIG. 2]

